CEMENT AND LIME
MANUFACTURE

"Cement and Lime Manufacture."

BEARING the title CEMENT AND CEMENT MANUFACTURE, this journal has since the year 1928 dealt with the scientific and mechanical problems associated with the manufacture, testing, and chemistry of Portland and other cements. Its popularity and the frequency with which its articles are quoted by other journals and authors are a measure of its success and of its usefulness to its readers in the cement industry.

Hitherto there has been a scarcity of published information on lime. Until recently the production of lime followed traditional custom, and there was perhaps little need for the subject to be dealt with at regular intervals. Nowadays, however, the tendency is to concentrate manufacture in large works using new types of plant and scientific methods of control, and it is felt that the time has arrived when the developments taking place throughout the world should be made known to the industry. So many cement manufacturers are also interested in lime that it is thought this could be most conveniently done by covering both subjects in one periodical. Science has no secrets; it welcomes publicity and, indeed, only flourishes by free interchange of opinions and ventilation of ideas. It is the arena for these that this journal now seeks to provide in the interests of both cement and lime.

The traditional ancestry of lime is illustrated by the terms that are employed in connection with it. Such terms as "lime burning," "lime slaking," "fat lime," etc., are inheritances from ancient times and their meanings are not self-evident to the layman or student who is better acquained with their equivalents of "calcination," "hydration," and "high-plasticity lime." In building practice the old terms of "fat lime," "mellow lime," "stone lime," "white lime," "grey lime," etc., must give place to those which are informative as to the precise qualities of the material. There is no doubt that these terms will soon be obsolete, and there will be three classes of lime known as "high calcium," "feebly hydraulic," and "eminently hydraulic."

In the building industry traditional methods have been revised during the past few years and partly replaced by new methods to satisfy the modern desire for speed. No longer is it practicable to specify months, or even weeks, for the slaking of lime, and both manufacturers and users have had to adapt themselves to modern requirements of minimum labour and maximum speed. The slaking of lime is a work requiring knowledge of the type of lime being used, and when local building employed local lime and local labour such knowledge was available. But now lime can be cheaply transported for long distances, and when a labourer, accustomed to only one type of lime, is required to slake either of the other types, the results are frequently unsatisfactory. This is one of the reasons why ready-slaked or hydrated lime is so rapidly increasing in popularity. There was, indeed, a tendency to rule out the use of lime when it was only obtainable in lump form because of the space and labour required for its slaking, and to adopt cement in its place for brickwork mortar. The supply of hydrated lime in bags has removed this obstacle, and there is now a definite return to the use of lime mortar.

To speed up construction a mortar which hardens more rapidly than lime is necessary, and for this purpose incorporation of cement in mortar is becoming a widespread practice. Lime manufacturers have also been stimulated by this desire for speed, and the production of semi-hydraulic lime which contains in itself hardening elements has developed. It is probable that eventually hydrated lime will entirely replace lump lime in the building industry.

There are other problems for the manufacturers in connection with lime for chemical purposes and for the paper, leather, and other industries. Some of these call for slow-setting milk of lime, others for lime of quick-slaking properties, and so on. The older methods of calcining lime, involving alternate layers of limestone and fuel in a kiln that depends upon atmospheric conditions for providing the draught which governs the rate and intensity of combustion, do not lend themselves well to the production of lime of controlled properties. Hence manufacturers have been compelled to adopt new methods involving temperature records and control, gas burning, etc. The slaking or hydration of lime by the manufacturer must also be treated as the chemical process that it actually is. Even lime for agricultural purposes has not been able to escape the control of science, and purchases of lime by the farmer and horticulturist are now governed by chemical analyses and tests under the Fertilisers and Feeding Stuffs Act.

Lime has this in common with cement, that there is still much to be learned about its manufacture and the chemistry of its setting and hardening. The thermal efficiency of lime kilns is hardly better than that of cement kilns, and there is no doubt that improvements will be made and published in this direction during the next few years. The reason for the hardening of lime may be the simple one of slow conversion to carbonate, but the hypothesis that gel desiccation plays a part still persists. It is, however, the impending advent of a standard specification for lime that is providing the most powerful stimulant to makers and users to abandon tradition and utilise scientific knowledge. The knowledge

gained by laboratory workers that the properties of lime, its plastering qualities, strength, and freedom from undesirable behaviour can be measured has provided the foundation for a standard specification which will be of immense service to architects and builders, and will also protect manufacturers from unfair competition from materials which can be classed as lime but which may be far from the 100 per cent. perfection which is expected. A new specification will also differentiate between the classes of lime and will be a means of educating users in the selection of the most suitable variety for their particular purpose. Much laboratory work has, however, still to be done to duplicate the conditions of building practice where lime mortar is always applied to a more or less absorbent surface which seems to play a part of supreme importance in determining the strength and stability of the mortar.

In conclusion, it must be pointed out that it is not our intention to give less space to cement. The articles on lime will be additional to the usual number of pages devoted to cement in the past, and in this way it is hoped to make the journal more useful to its present readers as well as to cater for the lime industry.

Radiated Heat for Primary Air.

AN interesting experiment is being made on the preheating of primary air for one of the kilns of the Republic Portland Cement Co., at Longhorn, Texas, using heat radiated from the shell of one of the rotary clinker coolers. Previously, states *Rock Products*, primary air had been introduced to the kiln at atmospheric temperature. The cooler is an Allis-Chalmers machine, 100 ft. long by 10 ft. diameter. A jacket of 16-gauge steel, 18 ft. long, has been built to enclose the cooler over the lifter section at the end of the brick lining. There is a 12-in. air gap between the outside of the cooler and the jacket. Metal straps at the ends of the jacket permit a tight fit.

The system is so constructed that air at atmospheric temperatures is drawn through the gap between the cooler shell and the jacket through four 12-in. by 20-in. adjustable openings below. In order to reach the fan on the kiln floor above, this air circulates through the air gap between the cooler wall and the jacket. Radiated heat from the hot zone of the cooler raises the air from atmospheric temperature to approximately 275 to 300 deg. F. before it is taken through pipes to the kiln as primary combustion air. The air, being heated from the exterior of the cooler, is dust free and consequently has no destructive action on the fan blades.

The installation has not been in use for a sufficient length of time to determine accurately the results, but a considerable saving in fuel has been effected, and no harmful effects on the temperature and quality of the clinker as coming from the cooler have been observed. Approximately 48 per cent. of the air necessary for combustion in the kiln is primary air, representing 13,000 cu. ft. per minute drawn through the improvised preheater. The kiln is 11 ft. in diameter and 250 ft. long.

The Design and Operation of Modern Lime Works–I.

By N. V. S. KNIBBS, D.Sc.

Introduction.

IT is the intention of this series of articles to discuss the design and operation of lime works and the factors which influence their construction and operation. This first will be largely concerned with clearing the ground for subsequent articles, and is therefore somewhat theoretical.

Lime-burning has been an important industry for thousands of years and, like most ancient industries, it is characterised by the conservatism of the methods used, which also often differ fundamentally in passing from one locality to another. The modern technologist is apt to dismiss such old practices as valueless, but a careful study generally shows that they have a sound basis and an historical study may reveal a reason for special methods and point the way to a sound modern technique. Unfortunately there is very little information available about the origin of lime-burning practices, but something may be learnt from old kilns still standing and from other sources.

There is little interchange of information between lime manufacturers, even to-day. Methods of winning the stone, crushing it, etc., are freely discussed, but burning methods are seldom ventilated. Possibly because of this reticence the technical literature still contains much misleading information about lime production.

English and United States Practice Contrasted.

A comparison of lime-burning practice in the United States and in England is interesting and informative. In England the mixed-feed kiln is used in the majority of plants. Gas-fired plants handle an important and increasing tonnage —upwards of 1,000 tons a day—and there are several Hoffmann kilns with direct firing. Rotary kilns are few in number and confined to the reburning of sludges, and other types are of negligible importance. In the United States the majority of kilns are furnace-fired—vertical shafts with fire-boxes built on to the sides, a type not used in England—whilst mixed-feed kilns in the United States are very seldom used for supplying lime to the ordinary market. Gas-fired kilns are fairly numerous and increasing, and there are many rotary kilns.

Furnace-fired kilns are built only in small units and the large United States plants seem, to English eyes, to have a countless number of kilns. Their capital and running costs are both higher than those of mixed-feed kilns, and one would therefore expect very great advantages in other directions to compensate for the obvious demerits. In my opinion, the reason for existing United States practice is largely an historical one. Lime-burning, in all countries, was originally carried out with wood as fuel. In England wood became scarce and was replaced by coal or coke hundreds of years ago and long before the Industrial Age called for large outputs. In the United States, on the other hand, wood was the staple fuel until comparatively recent years, and wood-burnt lime set a standard that was generally known. Furnace-fired kilns burning coal are a direct adaptation

of similar kilns burning wood. They produce lime which, though inferior to wood-burnt lime, is much closer to it in quality and appearance than lime produced in mixed-feed kilns. To change to the more efficient mixed-feed kiln would have meant not only a complete change of technique in a conservative industry but also the necessity of persuading a reluctant consumer to alter his ideas about what constitutes a good lime.

The United States tendency to standardisation has helped to perpetuate the use of furnace-fired kilns, and a very large proportion of the total output of lime there is made in a few types of these kilns. In contrast, the varieties of mixed-feed kilns used in England are legion, and they vary greatly in design.

In the hydration of lime the differences in method are not pronounced. With some notable exceptions English practice has followed that of the Continent or of the United States, even where the latter was especially designed to deal with a type of lime—the Ohio dolomitic lime—requiring somewhat different treatment from nearly all English limes.

The Theory of Lime-burning.

Readers of these articles are assumed to be familiar with the fundamental data of lime-burning. Nevertheless, because technical writers have often applied some of these data incorrectly to practical lime-burning conditions, it is necessary to discuss them briefly here. For convenience the fundamental thermal data for calcium carbonate and oxide are collected together in *Fig.* 1.

For discussion here it will be assumed that the limestone burned is practically pure, so that it may be taken as pure calcium carbonate with little error. Such stone requires theoretically 760 C.H.U. (1,368 B.Th.U.) per lb. of lime to change it in to lime and carbon dioxide gas. The fuel used to calcine it will be assumed to be coke or coal of 7,230 C.H.U. (13,000 B.Th.U.) net calorific value. It is therefore theoretically possible to calcine it with 0.105 of its weight of fuel, or a lime : fuel ratio of 9.5 : 1. Writers on lime-burning generally seem to assume that this theoretical figure may be approached as closely as may be desired by insulating the kiln, by complete combustion of the fuel, and by having adequate stone-preheating and lime-cooling space, but this assumption is incorrect, as the following argument will show.

Fig. 1 shows the dissociation pressure of calcium carbonate. In an atmosphere containing 40 per cent. carbon dioxide (the approximate amount in a very highly efficient kiln) it will dissociate at about 835 deg. C., at which the dissociation pressure is about 300 mm. Actually, immediately a piece of stone has a thin skin of lime its further dissociation requires a temperature of 900 deg. C., because it occurs in an atmosphere of carbon dioxide diffusing outwards through the pores of the lime. In a lime kiln, therefore, the heating medium is effective in inducing calcination only down to about 900 deg. C. Below that temperature, apart from an infinitesimal amount of " skin " calcination, the only effective work that the heating medium can perform is in raising the temperature of the stone to 900 deg. C. Now, the thermal units required to heat the stone to 900 deg.

DISSOCIATION PRESSURE OF CALCIUM CARBONATE.

HEAT OF DISSOCIATION OF CALCIUM CARBONATE.

AT 25°C. -42,600 CALS.
per MOLE. =
-760 C.H.Us. (1368 B.Th.
Us.) per LB. CALCIUM
OXIDE.

AT 900°C. -38,900 CALS.
per MOLE. =
-694 C.H.Us. (1249 B.Th.
Us.) per LB. CALCIUM
OXIDE.

PRESSURE - MILLIMETRES OF MERCURY

TEMPERATURE - DEGREES CENTIGRADE

MEAN SPECIFIC HEATS - CALCIUM CARBONATE & OXIDE.

M. S. H. (0° - t°C.).

CALCIUM CARBONATE

CALCIUM OXIDE

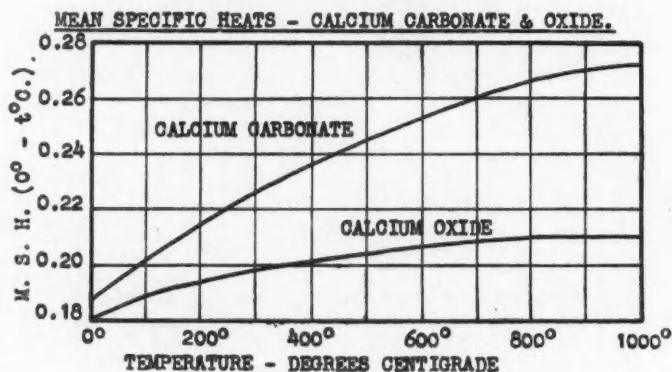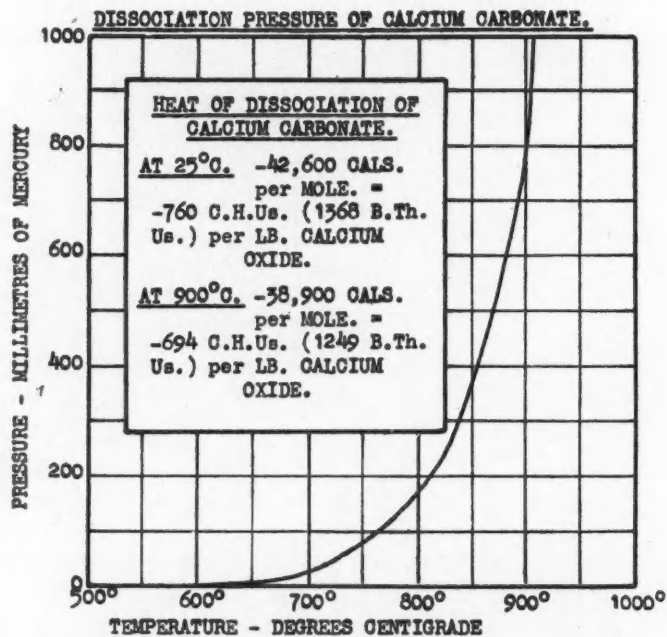TEMPERATURE - DEGREES CENTIGRADE

Fig. 1.

C. are $0.27 \times 900 \times 1.78 = 432$ C.H.U. (778 B.Th. U.) per lb. of lime. The heat required to calcine this lime at 900 deg. C. is 694 C.H.U. (1,249 B.Th.U.) per lb. of lime. That is to say, 1.60 times as much heat is required at or above 900 deg. C. as is required below 900 deg. C.

Consider what this involves in an actual kiln. The simplest instance is a furnace-fired kiln burning a short-flame coal where the lime is, in effect, heated by the hot gases. To attain 100 per cent. efficiency in such a kiln the hot gases would have to carry 1.60 times as much sensible heat above 900 deg. C. as below 900 deg. C., so that, allowing for increase of specific heat with temperature, a gas temperature of about 2,000 deg. C. would be required. This, of course, is utterly impracticable, both because the lime would be overburnt and because the refractory lining would not stand the heat. Therefore, even if all heat losses could be avoided, an efficiency of 100 per cent. would be impossible. The highest allowable temperature of the gases entering a kiln, burning pure stone and with a highly refractory and chemically suitable lining, is probably about 1,400 deg. C., at which temperature the maximum theoretical efficiency is about 55 per cent., or a lime : fuel ratio of about 5.2 : 1 with the above-mentioned fuel.

In mixed-feed and gas-fired kilns, and also to some extent in furnace-fired kilns using long-flame coal, the conditions are more complex. The hot fuel in a mixed-feed kiln radiates heat to surrounding lime, so that all the heat is not necessarily conveyed as sensible heat in gases. Nevertheless, in a kiln in which the fuel is charged in layers between layers of stone the heat used to calcine the bulk of the stone must be conveyed to it mainly as sensible heat, and the same argument holds good approximately. In a gas-fired kiln, designed so that all the air is drawn up through the cooling zone and all combustion takes place amongst the lime, conditions are rather different, because a long length of flame is possible where combustion and calcination take place together, but even here the same considerations apply after some allowance for flame length. In both instances the theoretically possible efficiencies are higher than the 55 per cent. given above for furnace-fired kilns; but probably they are never as high as 75 per cent. under the same temperature limitations.

We see, then, that the efficiency that may be attained in a kiln, apart altogether from avoidable heat losses, is limited by the permissible maximum temperature, and that no actual kiln could approach 100 per cent. efficiency even if heat losses were eliminated. In actual kilns there are various losses which, of course, reduce the theoretically possible maximum efficiency but which to some extent are controllable. These losses, and their control, will be discussed in subsequent articles.

Thermal Efficiency and Quality.

Since thermal efficiency increases with increasing temperature it would be advisable to operate kilns at the highest temperature that the refractory lining would permit, were it not that a high temperature decreases the quality of the lime. In furnace-fired and gas-fired kilns the damage is due to overheating

alone, which reduces enormously the rate of slaking of the lime, and in a mixed-feed kiln there is the additional deterioration from chemical contamination due to the fuel ash fluxing with the lime.   In all instances the degree of deterioration depends on time as well as temperature, but temperature is the more important factor.   In practical lime production there is always a compromise between quality and cost, the kiln being operated to give a reasonable fuel efficiency and sufficient output of a quality which is saleable but inferior to the best actually attainable.   The tendency to err on the side of inferior quality in the effort to reduce the cost of production to a minimum must be avoided.

This fundamental incompatibility of maximum fuel efficiency with highest quality does not seem to be generally recognised.   The optimum conditions, of course, vary widely with different classes of lime and different sizes of stone, but the prime difficulty remains.

The Rate of Burning of Limestone.

In spite of the economic importance of the lime-burning reaction the data on the rate at which calcination proceeds under any given conditions are meagre and conflicting.   It has been investigated theoretically and experimentally by Haslam and Smith (*Journal of Industrial Engineering and Chemistry*, 20, 170, 1928) and experimentally by Furnas (*ibid*. 23, 534, 1931) with very different results.   The former investigators found that the rate at which a piece of stone is calcined at any fixed surrounding temperature varies approximately as the square of the linear dimensions, so that a 6-in. lump of stone would take four times as long to calcine as a 3-in. lump of the same shape.   Furnas, on the other hand, found calcination to progress at a fixed rate at any temperature, so that the time of calcination varies as the linear dimensions, and a 6-in. lump takes only twice as long as one of 3 inches.

The experimental results of Furnas are explicable only if the rate of heat transmission through the lime is so rapid as to be of negligible importance compared with the rate of attainment of equilibrium at any temperature.   Dissociation is not instantaneous when the stone reaches or exceeds the dissociation temperature.   It has a definite velocity, which must be a function of the temperature and which will increase rapidly as the temperature of the limestone exceeds the dissociation temperature.   Furnas's work seems to show that there is a fairly wide range of temperature, up to about 950 deg. C., at which the stone is metastable.   Nevertheless, it seems unlikely that the rate of heat transference through lime has actually so little effect on the rate of calcination, and certain other work on the rate of calcination of English limestone (unpublished) gave results more in accord with those of Haslam and Smith than with those of Furnas.

The two authorities agree in finding a rapid increase in the rate of calcination with increase of temperature.   Furnas found the rate of calcination of stone surrounded by a temperature of 1,200 deg. C. to be 4.5 times, and of 1,100 deg. C. 2.1 times, as rapid as when the surrounding temperature was 1,000 deg. C.   The other investigators found a lesser effect of temperature, but in this instance

Furnas's results are more nearly in accord with the unpublished investigation mentioned.

Consider, now, the calcination of a piece of stone which has already been heated to about 900 deg. C. in the preheating zone of a kiln. Heat has first to be supplied to the outside of the lump, either by direct radiation from fuel or flame, or by heat transference from hot gases passing over the surface of the lump. The rate of heat transference will depend on the area of the lump exposed to radiation and gas contact, and also on the gas velocity. The acquired heat has now to pass through the lime already formed on the surface, and the rate of transfer will be a function of the thickness of the lime layer and the difference of temperature between the outside of the lump and the lime-limestone boundary, which latter will be close to 900 deg. C. (or, accepting Furnas's figures, between 900 deg. C. and 950 deg. C.). Finally, the dissociation reaction has to proceed at a velocity that will absorb all the heat arriving at the phase boundary, and this would appear to necessitate a temperature at that boundary above the equilibrium temperature, the excess being dependent on the rate of calcination.

In the burning zone of the lime kiln there are, therefore, three main thermal processes (apart from the actual heat production by the combustion of the fuel), namely, (1) Heat transfer from fuel or combustion gases to lime, (2) Heat transfer through the lime layer, and (3) Change of sensible to latent heat in the burning reaction. The first of these processes can to some extent be influenced by kiln design, and it is profoundly influenced by the size, shape and regularity of the stone. In mixed-feed kilns it is also influenced by fuel distribution and size. For a given size of stone the second is beyond control, but depends upon the quality of the stone. Lime from chalk, for example, has a lower conductivity than limestone lime. The average thickness of the layer, however, depends on the average size of the stone, and is therefore controllable by sizing the stone. About the third there is little information available. In practice, different stones of the same density seem to vary in the ease with which they may be calcined, and if this apparent difference is real it must be due to a difference in the rate of dissociation at a given temperature. The difference may conceivably be due to traces of impurities which catalyse the reaction, but there is no reliable information about the matter.

The Problems of Lime Plant Design.

Of the several operations involved in lime production the winning of the stone will not be discussed in this series, except in so far as it bears on other matters that are being discussed. The quarrying of limestone is already widely discussed, and progress in methods and plant is generally fully reported. The problems to be considered here are therefore those of kiln design, including loading, discharging, and firing arrangements ; the treatment of the lime produced, where necessary, to fit it for the market ; its crushing and pulverising to produce ground lime ; and the complete scheme of hydration of lime.

The modern tendency to centralisation and large units of production has not much affected lime manufacture, and the great majority of plants are still small.

C

Generally, therefore, the designer cannot follow the easy road to economy of simply increasing the size of his units and fitting them with labour-saving appliances. More often it is necessary to attempt the more difficult task of making small units efficient, and there is great scope for this in the lime industry.

The major problem in design is that of an efficient lime-burning unit which will burn the particular limestone with a fuel obtainable at an economic price and produce a lime of high quality, suited to the existing market. The extraordinary diversity of types of lime kiln in operation, even on any one kind of limestone, is evidence that none of the existing types is of predominant merit. Of course, there is a variation in the quality of lime required by different users, and one kiln may produce lime more suited to one use whilst another type may make lime better adapted to another market. It would be of great assistance if there were standard specifications for lime for all the major industries using it, but the difficulty in securing acceptance of specifications for building lime is not a hopeful portent. Without such official definition of what constitutes good lime there is a tendency on the one hand to insist on standards of no real importance, which often owe their origin to some local peculiarity of stone or method of burning, and on the other hand to accept anything as " lime " so long as it is usable and is lower in price than other supplies.

Sometimes extraneous circumstances determine the design of plant to be adopted. For example, at the present time, the great increase in a house building, together with the prosperity of the heavy industries, is in some districts favouring the introduction of gas-fired instead of mixed-feed kilns. Activity in the heavy industries has increased the price of coke, and in places house building has developed to the vicinity of lime plants, which may consequently be debarred from using bituminous coal in mixed-feed kilns on account of the smoke nuisance. In the same way, the dusty exhausts that are to be seen from some hydrating plants are not permissible where house property adjoins the plant, and this factor alone may be decisive in the choice of a plant.

The conditions to be satisfied in lime-plant design are therefore many and varied, and it is impossible to foresee all that may be encountered. Nevertheless, in subsequent articles it is hoped to touch on the major problems, and an attempt will be made to show how, in modern plants, they have been dealt with or how in the future the difficulties may be overcome.

The Problems of Lime-Plant Operation.

The problems encountered in the operation of lime plants are of two kinds. A well-designed burning plant may produce lime almost automatically once it is started, and operation problems are reduced to setting the controls to give the quality of product desired at the best possible fuel consumption. Such plants do not require especially experienced operatives to attend them. Most plants, however, and not necessarily the less efficient, are by no means so fully automatic, and fairly constant attention is needed to meet fluctuating conditions. Experience is then needed, and many kilns depend for their success on the life-long

experience of lime-burners, who generally appear to know instinctively what to do.

The fundamental problem in managing a lime-burning plant is to strike the most favourable balance between conflicting interests. High temperature, as already noted, gives high fuel efficiency, but low quality of lime and short life of kiln linings ; it also increases kiln output. The output of a kiln may also be increased by increasing the draught through it, and a high output generally tends towards higher fuel efficiency (since radiation and similar losses are reduced per ton of output) and, of course, it reduces depreciation and overhead costs. Increased draught, however, is generally obtainable only by using more power, and the power consumption goes up rapidly, its cost soon outweighing the saving effected in other ways.

Some hydrating plants also require experience in their operation, but there is little justification for designs which are not almost fully automatic. The quality of lime burnt from any particular stone can be judged fairly easily by inspection of a simple test, but this is not so with hydrate. No experience can distinguish between lime that is fully hydrated and some that is not quite hydrated, and there is no simple test that can be applied. A hydrating plant should therefore be capable of being set to produce the required product, and uniformity in the quality of the lime should be taken care of by the process itself. Apart from the experience needed in starting up the plant, the only problem in operation is to adjust the controls to meet alterations in the kind of hydrate that is required.

[To to continued.]

Impervious Lime Mortar.

LIME mortar in the hardened condition is much more porous than cement, because a colloidal mass is first formed which later changes to crystalline calcium carbonate due to the action of the atmosphere. Cement, on the other hand, commences with a comparatively coarse structure, a part of which later becomes colloidal and fills the pores by swelling. The colloidal mass of the lime mortar shrinks on conversion to calcium carbonate and leaves a porous structure. A step in the production of more impervious lime has been taken by the addition of water-repellent substances such as stearates and oleates in a fine state of division.

A method of rendering lime mortar waterproof consists in the mixing of vegetable fats and oils with finely-divided quicklime. When the lime is slaked the heat of slaking helps to make the lime mixture uniform and prevents the separation of the water-repellent substance. This method is said to have gained considerable success in the United States. The disadvantage is that, when the lime is stored in sacks, moisture from the air slowly hydrates the quicklime and there is a considerable increase in volume which causes the sacks to burst. This difficulty is removed by using watertight and airtight sacks consisting of several layers of paper and a layer of cellophane. In this type of packing, quicklime can be kept for more than two years without deterioration.— *Tonindustrie Zeitung*, 1936, p. 826.

A Modern Lime Works in Germany.

A NEW lime works recently erected near Regensburg in Germany, and having at its disposal an almost pure limestone, is described by H. Laeger in a recent issue of *Tonindustrie Zeitung*.

Fig. I shows the works just after erection.   Agricultural and building limes are burnt in circular and shaft kilns, and calcium carbonate is ground to various degrees of fineness.   Besides agricultural lime made to the Government specification, finely ground quicklime for building and very fine hydrated lime for chemical works are produced.


Fig. 1.

Large blocks of limestone from the quarry are tipped into a hopper from which they drop on to a band conveyor in controlled amounts according to the hardness of the stone and the capacity of the crushers.   The exit grids of the hammer breakers are easily replaceable so that the size of the crushed material may be varied as desired ; for instance, the limestone for hydrated lime is crushed smaller than that for ground limestone or quicklime.

The hydrating plant (*Fig.* 2) consists of three units which can be used alternately.   The total amount of water for slaking and its rate of flow are measured and regulated.   The flues from the hydrating plant are made of wood since iron would rust ; they keep the air free from dust and condensed steam.

Fig. 3 shows the emptying equipment below the six slaking silos. Specially constructed slides and compartment wheels afford a uniform draw off. The completely slaked material is collected by a screw conveyor and fed by bucket elevator into a large bunker which supplies the mills. A second bunker of the same size is mounted over the mill and can be fed by both the bucket elevators

Fig. 2.
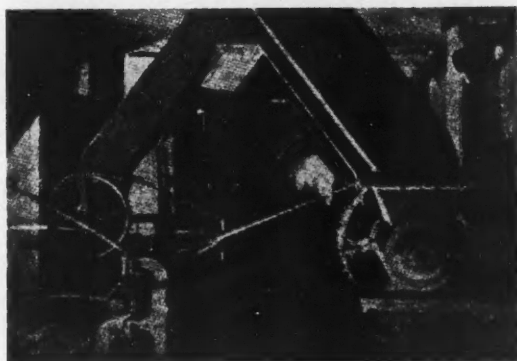
Fig. 3.

behind the crushers. This cross connection in the feed equipment enables slaking and the preliminary grinding of limestone and unslaked lime to be carried out simultaneously.

On account of the varied material air-swept ring roller mills (*Fig.* 4) are used in which damp limestone using heated air, quicklime, and slaked lime can be

ground to widely different finenesses. The feed equipment, which is separate for lump limestone and fine slaked lime, is driven by direct-current motors which can be regulated within wide limits so that unavoidable variations in the character of the feed can be compensated and the mill run at its highest efficiency. The dust separators hang above the fine-material screw conveyor over the five silos for the finished product.

The output of the grinding plant is from 5 to 8 tons per hour of limestone, 8 to 12 tons per hour of quicklime, and 12 to 20 tons per hour of ground slaked
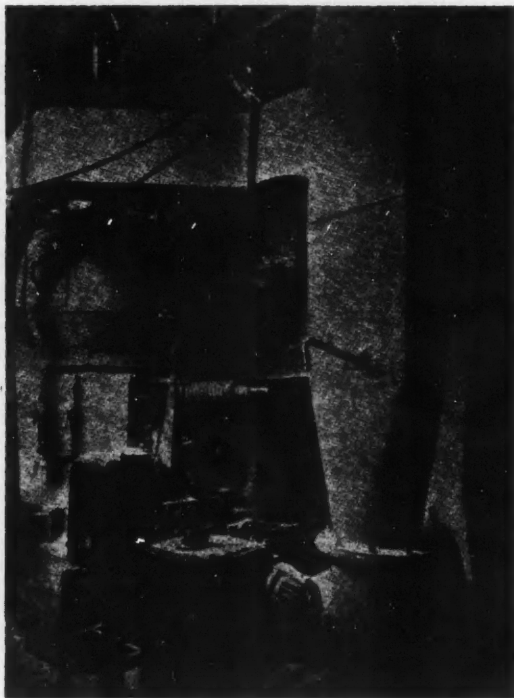

Fig. 4.

lime. The capacity of the other machines is somewhat greater, so that it is necessary to run them only intermittently according to the requirements of the preliminary grinding plant and the packing department.

The various supplementary machines such as conveyor screws, etc., are driven individually by thirty motors delivering altogether 400 nominal horse-power. Since these work only as required, the actual power consumption can be kept down at a low figure. A substation, with a capacity of 600 kVA. to allow for possible expansion of the works, supplies the power.

Reconditioning Portland Cement Deteriorated by Prolonged Storage.

By PROFESSOR B. G. SKRAMTAJEV.

CENTRAL INSTITUTE FOR BUILDING RESEARCH, MOSCOW.

THE following is abstracted from a report submitted by the author to the Central Institute of Chemistry in Moscow in July, 1935, and may serve to supplement the paper on " The Carbonation of Unhydrated Portland Cement " published in the September 1936 number of your journal.

The factors responsible for the deterioration of cement stored for long periods are well known. Primarily, the moisture contained in the air affects the cement in the same way as the mixing water, hydrate and hydrosilicate of lime being slowly formed on the surface of the particles. The cement particles are also subjected to the action of carbon dioxide in the air, which changes the calcium hydroxide into calcium carbonate and the hydrosilicate of lime into calcium carbonate and amorphous free silicic acid, the result being that the particles become coated with an insoluble complex film of these two substances. This film prevents the combination of the cement with the mixing water in the process of making concrete or mortar, especially when the mixing is gentle and no vigorous mechanical stress is exerted upon the film.

These phenomena explain why cements after prolonged storage (up to one year) lose up to 40 per cent. of their original quality. The reduction in quality is more marked in practical concrete than in mortar made in accordance with a standard test, because five minutes' mixing by the method laid down in the standard test is more effective than the process of concrete mixing in breaking the films.

It was proposed to improve cement deteriorated after storage by adding a weak solution of hydrochloric acid to the mixing water, with the object of destroying the carbonate content of the films on the cement particles in accordance with the formula :

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

This addition allows the water to reach the unaltered cement particles and thus restores the quality of the cement, while calcium chloride accelerates the hardening. Calcium chloride by itself does not hasten the hardening of cements which have deteriorated due to prolonged storage, as it is unable to destroy the carbonate films.

Generally speaking, hydrochloric acid is a good accelerator of the hardening of cements, as was shown by the results of some of my recent investigations published in the Soviet journal *Cement* (No. 2, 1935), and the German journal *Bautenschutz* (No. 7, 1935). But here we are dealing with the special case of hydrochloric acid affecting the quality of aged cement. The conclusions reached by us have been verified by the following tests :

(1) Cement has been artificially " aged " by passing a current of carbonic acid and water vapour through it by means of the apparatus shown in *Fig.*1. The first test was undertaken with the object of determining the degree of diminu-
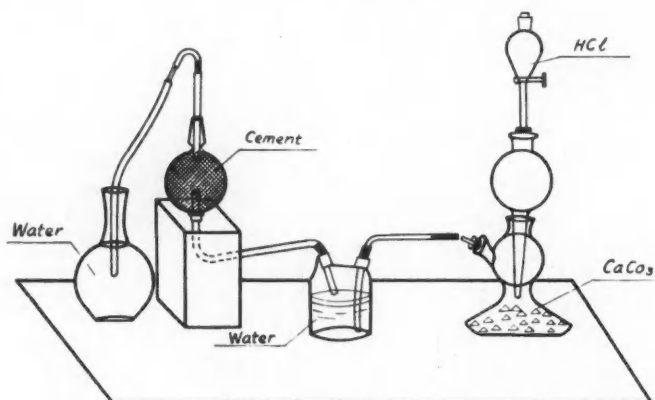

Fig. 1.

tion of the cement strength after thirty hours' treatment. This test produced the following results :

	Compressive strength in kg. per square centimetre of 1 : 3 mortar.		
	After 4 days	After 7 days	After 28 days
Fresh cement	163	159	273
Treated cement	62	105	138

(2) In the second test artificially " aged " cement was mixed with a 4 per cent. solution of hydrochloric acid, with the following result :

Compressive strength in kg. per square centimetre of 1 : 3 mortar.		
After 4 days	After 7 days	After 28 days
119	178	227

The possibility of improving spoiled cement by means of hydrochloric acid has thus been proved by use of a 4 per cent. solution ; a stronger solution might be used if this were possible within the setting time of the cement.

Refractory Linings of Cement Kilns.

THE choice of a refractory lining for a kiln is important, especially when high-strength and special cements are being manufactured. The possibility of manufacture at an economic cost often depends largely on whether a suitable refractory substance can be obtained. The question of refractory linings for cement kilns is examined by D. Steiner in a recent number of *Zement* (1936, p. 619), and the author deals with the extent to which the refractory industry can fulfil the special requirements of the cement industry. The following is a translation of the article.

At the present time only the rotary and automatic shaft kilns need be considered. The heat distributions in the two cases are similar, namely, a preheating and calcining zone, followed by a sintering zone where the temperature is highest, and a cooling zone. The conditions which must be fulfilled are, however, different in each zone, but the zones cannot be sharply differentiated. The divisions are better made according to the chief reactions which predominate in the zone considered. The zones overlap each other so that calcination begins in the preheating zone, and the calcinating and sintering zones cannot be properly separated. The three divisions are useful in practice because the requirements in each zone are so fundamentally different that up to the present the lining in each case has been of a different material for economic reasons.

The difference between rotary and shaft kilns occurs in the different requirements from the bricks and in the size of the zones. In the rotary kiln a pre-heating zone of more than two-thirds of the length of the kiln is followed by a sintering zone from 4 to 8 metres long and a very short cooling zone, and the clinker is finally cooled in a separate cooler. In the shaft kiln, the preheating zone is extremely short (only 1 to 2 metres long), the sintering zone is very much longer, and the cooling zone is about two-thirds of the total length ; no separate cooler is used, and the kiln shaft acts as a cooler.

There is a great difference in the speed of the material in the two cases, and this makes different types of fire-brick necessary. In the shaft kiln the brickwork is at rest and holds together even if comparatively poorly built, while in the rotary kiln the brickwork will be stable only if very carefully constructed. The raw material moves along the shaft kiln at a speed of only 0.5 to 2 metres per hour, while in the rotary kiln speeds of 500 to 700 metres per hour are usual. As the raw material traverses a spiral path in the rotary kiln every portion of it has an opportunity of coming into contact with the brickwork ; in the shaft kiln only the clinker on the outside slides on the brickwork. Hence it would seem to be necessary to use a higher quality brick for rotary kilns, but this is not so since only about one-tenth of the kiln cross section is filled with material and the small weight of clinker causes little attrition. On the other hand in the

shaft kiln, especially in the cooling zone, a large portion of the clinker exerts pressure against the brickwork.

Rotary-kiln clinker is usually spherical in shape, and only occasionally do large crusts, or angular or heavy pieces of clinker, rub against the walls. In the shaft kiln, however, all the clinker has sharp corners and edges. The tendency to " ball " plays an important part and, except for ring formation in the pre-heating zone, will be taken into consideration only in the sintering zone. In the shaft kiln sticking can reduce the life of the lining considerably. In the rotary kiln sticking may form coatings which, when they fall off, damage the brickwork, but a good coating is desirable and forms the basis of the stability of the lining.

The problem can be simplified since good clay fire-brick lining can be chosen for the preheating and cooling zones. Difficulties arise only in the sintering zone. On account of the very much smaller amount of brick required for shaft kilns, there is a tendency to line the whole shaft with the same brick and hence to increase the cost. According to modern practice, however, the dearer sintering zone lining is not so suitable for resisting attrition in the cooling zone as a much cheaper, less refractory, but more resistant clay-brick lining.

In the preheating and transition zones in the rotary kiln and the cooling zone in the shaft kiln the most suitable material is a hard-burnt clay fire-brick of about cone 30 to 32, with about 35 per cent. Al_2O_3, a compressive strength of 400 to 500 kg. per square centimetre, and not too low a porosity. For the transition zone, where there is occasionally a high temperature, cone 35 to 36 and 40 to 42 per cent. Al_2O_3 are required.

In the development of the lining of rotary and shaft kilns the following chief phases are evident. Up to the present, first-class clay fire-bricks have been used in shaft-kiln practice. For normal working and with good outer walls, especially with good close jointing of the bricks cut to the radius of the kiln, a life of about one year can be obtained. This is sufficient, since the kiln must be overhauled during its stoppage in winter. Where the kiln walls must be renewed sooner the trouble is due, not to the fire-brick, but to the method of working, and improvement has resulted from preventing sticking and working the kiln with high air pressure and a shorter time of passage for the material. It is only very seldom in the case of shaft kilns that the linings are replaced by the types described later.

In rotary kilns the best clay fire-brick lining will be completely destroyed in the sintering zone. Generally such a lining must be renewed every one or two months, and this, due to the cost of materials and labour, heat losses, and production losses, causes a reduction in efficiency far greater than is usually admitted. So long as no other material is available this short life is a necessary evil. In specially favourable circumstances and with good raw material, a life for the lining of six to twelve months can be attained by careful running of the kiln. In these circumstances a clinker coating will have been burnt on to the fire-brick.

It was, therefore, a short step to leaving out the fire-brick and lining the

sintering zone of the rotary kiln with clinker. In practice, v. Valeur's patent for clinker concrete for rotary kilns has attracted great interest. Compared with clay fire-brick it affords a distinct economy so long as the clinker concrete is made on the works. The saving is deceptive when only the price of the brick is compared, and most works have abandoned clinker concrete. In the best cases the stability of clinker concrete can reach that of good clay fire-brick, but this can never satisfy an up-to-date works.

A better kiln lining is necessary in the production of high-strength cement and certain special cements. In this connection the refractoriness of the fire-brick has been increased by increasing the basic portion (Al_2O_3) with the idea that good chemical resistance will be obtained only if the lining, which has to withstand the action of a very basic cement clinker, is basic also. Acid linings can have as high a refractoriness, but will be destroyed by the clinker in a very short time.

Up to a short time ago a highly basic lining for the sintering zone of a rotary kiln was universal. It contained 60 to 70 per cent. or more Al_2O_3 and had a seger cone figure of 38 or higher. Especially important was the correct particle size distribution of the aggregate, and there have been failures of fire-bricks whose composition was apparently suitable. Included among the bricks which have proved good are Alumidon-Dynamidon bricks made in Germany or Switzerland, the Thuringia bricks from the Didier Works in Germany, and the American Arcofrax bricks ; the last have been used all over the world. The Czecho-slovakian Uramidon and Suprauramidon have not been tested in cement kilns. A pure fused corundum under the name " Korhard " has been recommended for cement kilns ; so far as the writer is aware, it is not yet certain that this affords all the requirements for several reasons, which will not be gone into in this paper.

The stability of highly basic bricks is a good deal better than that of first-class clay bricks, and their life in the sintering zone is two, three and more times as long. A strongly basic lining of this type is therefore often chosen ; it is, however, already being replaced by magnesite bricks on account of their highly suitable characteristics.

For the last twenty years the use of magnesite bricks in rotary kilns has been discussed, but two objections have been raised. First it was feared that the lining would give up MgO to the clinker, whereby the composition would be altered with the danger of magnesia unsoundness. Even for small stability, however, the amount of MgO given to the clinker is of no importance. The second objection was that magnesite bricks were very sensitive to changes of temperature, but it has been found possible to produce a magnesite brick which has good refractory properties and is stable when subjected to temperature changes. The pioneer work in this direction was carried out by the Österreichisch-Amerikanischen Magnesit A.G., at Radentheim, in Austria, where suitable raw material deposits were available. Another firm which produces a good magnesite brick is the Westböhmische Kaolin und Chamotte-Slovakische Magnesit-Werke, of Prague. The properties of Radex and Lovinit bricks (the trade names of these firms) are very much alike, and differences only will be pointed out.

The following are the compositions of Radex and Lovinit bricks delivered at the same time :

					Radex Per cent.	Lovinit Per cent.
SiO_2	..	..	..	..	1.90	2.10
Al_2O_3	..	..	..	..	7.30	4.66
Fe_2O_3	..	..	..	..	3.40	6.84
CaO	..	..	..	..	2.50	2.60
MgO	..	..	..	..	84.22	82.80

As can be seen the materials consist mostly of MgO, the rest being an iron-rich bauxite. It may be noted that in Radex Al_2O_3 predominates while in Lovinit, Fe_2O_3 predominates.

The refractoriness corresponds to cone 42 or higher, and hence the bricks have a larger reserve so far as resistance to temperature is concerned. In the spalling test, the bricks withstand 70 to 80 cycles or more. Hence kilns lined with Radex or Lovinit can be stopped and restarted without the bricks being damaged. Slight after-shrinkage in the kiln, especially at high temperatures and after long times of heating, has not been completely eliminated.

When working with a reducing flame, cracks can often be seen in the brickwork after stopping the kiln, but these can easily be filled. The manufacturers are, however, trying to eliminate completely this small shrinkage by burning the bricks sufficiently hard. The iron content also should be kept at a low limit.

As the action of the clinker on the brickwork is of great importance, a standard method of testing has been devised. When Radex and Lovinit are compared with high-alumina clay bricks it can be seen that the former possess a very much greater resistance to attack. This would suggest that these bricks have an unlimited stability in the kiln, but stability is governed by factors which do not appear in the laboratory test. In the rotary kiln Radex and Lovinit form excellent coatings, and it is primarily due to the coatings that the bricks are stable. If the coating falls off, or if the kiln is operated so that a very thin coating is formed, the magnesia bricks are subjected to mechanical abrasion so that their stability is no better than that of a clay brick. In the Unax cooler, where no coatings are formed, the magnesia brick wears much more quickly than clay brick. This point must be stressed as it may be considered that a coating is not important in the case of Radex or Lovinit bricks, whereas by using an insulating layer between the lining and the shell a good coating may be obtained. A good coating can be obtained with these bricks, in spite of the fact that they are very resistant to the action of clinker, because there is a fusion of the clinker at the surface of contact with the brickwork and part of the molten material soaks into the brickwork, or at least sticks so fast that it forms a good coating without chemical action.

The conductivity of magnesite bricks is considerably greater than that of clay bricks, as can be seen from the following table :

| Deg. C. | λ in Cal. per metre per hour | |
	Clay brick.	Magnesite.
500	0.72	7.0
700	0.82	5.2
900	0.9	4.0

The negative temperature coefficient of the magnesite brick is an advantage, but the absolute value of the heat conductivity is so great that all the advantage is on the side of the clay brick. It would, therefore, be considered that in the case of somewhat thin walls and no insulation of the shell, it would be impossible to obtain uniform working with magnesite bricks.

Radex and Lovinit give somewhat better figures, as follows :

Deg. C.	λ
500	2.60
1,000	1.80
1,500	1.50

In any case the heat conductivity at the temperatures under consideration is about twice that of clay brick. This disadvantage can be removed by suitable insulation, which should lead eventually to a lower heat loss than in the case of clay bricks. Clay bricks cannot be insulated, because they will not withstand the heating conditions produced thereby. The result is that, in spite of the greater heat conductivity of Radex and Lovinit, a lower shell temperature can be obtained than with clay bricks. This results in a saving due to lower radiation losses.

Insulation of the brickwork makes it possible to use a very much smaller thickness of magnesite brick. If a kiln with a Lovinit lining and an insulating layer is compared with a kiln having a clay-brick lining of the same thickness, and the conditions at first are such that the shell temperature and the heat loss are the same, the difference is very marked, especially over a period of a year or more. Under these conditions there is very small wear of the Lovinit lining and therefore only a small gradual increase of the heat loss, while in the case of the clay-brick lining there is great wear and an increasing heat loss. A Lovinit lining has several times the life of a clay-brick lining, and the effects of this are shown in Figs. 1 to 4.

The necessary condition to obtain this advantage is suitable insulation, and the insulating bricks must give good insulation, have sufficient strength, and have sufficient refractoriness, especially when the inner lining is reduced in thickness. With a well-insulated kiln there is less need to depend on the skill of the burner than in the case of kilns which are not insulated.

The temperature in the sintering zone can be somewhat higher without ill effects so that, with a slightly greater heat loss, good clinker can be produced when the coal drops in quality or the composition of the raw material changes. If burning is carried out at the lower limit of temperature then variations, which
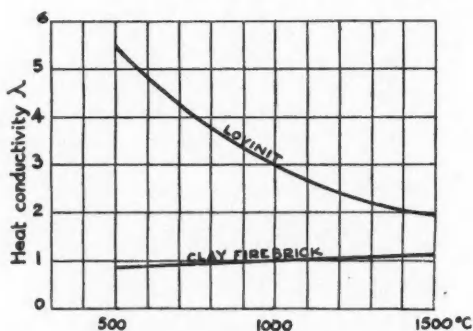
FIG. 1.—Heat Conductivity of Clay Firebrick and Lovinit
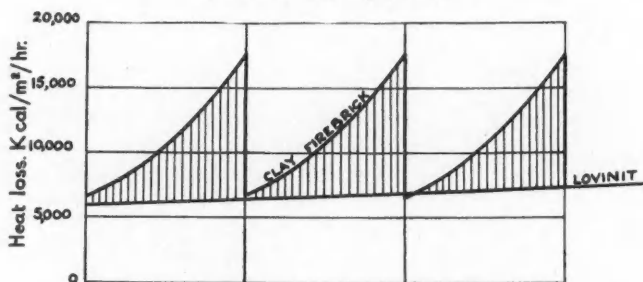in Relation to Temperature.

FIG. 2.—Comparison of Heat Losses of (a) Insulated Lovinit
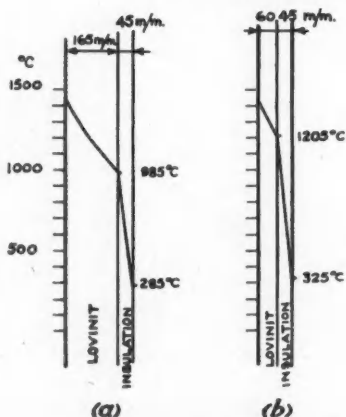Lining and (b) periodically renewed Clay Firebrick Lining.

FIG. 3.—Temperatures in an Insulated
Lovinit Lining 165 mm. thick (a) at
the start, (b) when the Lining had worn
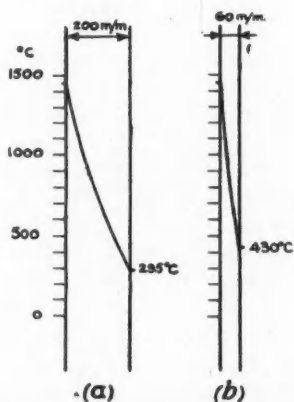to a thickness of 60 mm.

FIG. 4.—Temperature in a Clay Fire-
brick Lining 200 mm. thick (a) at the
start, (b) when worn to a thickness of
60 mm.

cannot be immediately corrected by the burner, will most certainly cause under-burning or clinker rings in the kiln.

The specific gravity of magnesite bricks which are resistant to temperature variations is 3.5 to 3.55 ; the apparent specific gravity is 2.87 to 2.90, which corresponds to a porosity of 10 per cent. by weight of water. The brick is therefore about 15 per cent. heavier than good refractory clay brick. The extra cost of the greater density can be reduced by using a thinner lining, but in the long run the extra cost of a lining of full thickness is set off by the cost of renewing the thinner lining. Porosity reduces the heat conductivity of the brick, but it is an unwanted characteristic, especially as the pores get filled with flue gas and there may be separation of carbon or sulphur inside the brick. The permeability of the brick depends not only on the total number of pores, but chiefly on their shape and distribution, so that for the same porosity magnesite is only half as permeable as clay brick.

The compressive strength (cold) for Lovinit and Radex is given by the makers as 460 kg. per square centimetre. Even if the strength were less it would not be of such importance as the compressive strength at the sintering zone temperature. It is necessary to remember that the strength falls very considerably if the bricks are stored in the open, and a small amount of moisture has a very bad effect ; a magnesite brick lining must therefore be built dry.

The thermal expansion of Lovinit is 0.80 per cent. at 1,000 deg. C. and 1.20 per cent. at 1,500 deg. C. This is about twice the expansion of clay brick but less than ordinary magnesite brick. By suitable grading of the particle sizes during manufacture of the brick it is possible to reduce the expansion, but this factor must be considered when installing the lining. In the case of a kiln of 3 m. diameter there is an expansion of about 10 cm. at the sintering zone temperature, and this must be allowed for if the bonding of the brickwork is to remain, or spalling of the bricks on account of internal stress is to be avoided. This, however, does not lead to any very great difficulties when erecting the lining.

A good lining must be satisfactory in every respect so far as refractoriness is concerned, and there must be sufficiently good insulation. As Radex and Lovinit fulfil the first condition only, the question of insulation must be considered. The magnesite bricks may be laid dry with sheet-iron plates between each brick for jointing. At sintering temperature the iron melts and is absorbed by the brick, forming with the outer layer a monolithic structure which allows for normal heat expansion. The Westböhm insulating brick is a basic clay brick of over cone 30, so that it can be used with a very thin magnesite brick lining and remains good with extensive wear of the inner lining. This brick has a porosity of 70 per cent. for an apparent specific gravity of 0.7, and the heat conductivity at normal temperatures is 0.2 or 0.4 at about 1,000 deg. C. It also has sufficient strength to withstand the stresses imposed on it in the kiln. The insulating bricks are laid in refractory cement in such a way that the whole fits to the kiln shell and the magnesite without any discontinuity. In this way movement of the insulating layer against the magnesite brick is avoided ; this is very important, since otherwise the insulating layer would fall to pieces.

The Hardening of Lime Mortar.

EXPERIMENTS which have led the author to the conclusion that the carbonation of lime in lime mortar is not the chief source of the latter's strength are described by V. Rodt in *Tonindustrie Zeitung* (1936, pp. 97, 539). It is pointed out that the standard strength tests are carried out one and four weeks after gauging when the specimen has taken up very little carbon dioxide from the atmosphere, which contains only 0.02 to 0.03 per cent. by volume. Tests carried out by the author show that lime mortar which has been cured under the same conditions as in the standard test but with the exclusion of carbon dioxide has a similar strength. He shows also that hardening cannot be due to a reaction of lime with sand to form calcium silicate.

Strength tests on silica, alumina, and iron oxide gels with varying water contents are given, and it is shown that they all exceed that of hydrated lime.

The author suggests that the hardening of lime mortar occurs as follows : The calcium hydrate gel in the mortar shrinks with loss of water during the drying of the mortar, and thus gains strength slowly. This shrinkage makes the sand grains adhere together, and they are bound together with a kind of mineral glue, the hardening of which is due to the shrinkage of the colloidal calcium hydrate combined with the adhesion forces which are called into action thereby. As would be expected if this were true, the mortar will not harden if it is kept in a saturated atmosphere where drying cannot occur.

It is suggested that if the strength of lime mortar is due to the formation of calcium carbonate, then the addition of this substance finely ground to the mortar should increase its strength. Actually this does not occur. A lime-mortar specimen was kept in a stream of carbon dioxide saturated with water vapour for several months in such a way that no drying could take place ; under these conditions the specimen remained soft. If, however, alternate drying and exposure to carbon dioxide is applied a very high strength is obtained, which is in accordance with the author's theory.

The conclusion drawn from the vapour-pressure curves of hydrated lime is that a colloidal product is obtained when lime is slaked. Curves are given showing the relation between compressive strengths and water contents of various gels.

In the same journal (1936, p. 761) W. Dawihl, R. Flüshöh and K. May express their disagreement with the foregoing views regarding the colloidal character of slaked lime. They point out that the shrinking and swelling of lime mortar are phenomena associated with the fineness of the particles, which need not be of colloidal dimensions. X-ray crystal analysis of slaked lime made from marble shows a crystalline and not an amorphous structure ; also, the sharpness of the lines in the photographs indicates that, though the crystals may be sub-microscopic, they are not an exceptionally small-sized representative of this class. The conclusion arrived at is that it is not the colloidal character of slaked

lime that is responsible for hardening but the microscopical fineness of its particles. Details of experiments by these authors are given in which the speed of slaking was retarded by the use of a mixture of methyl alcohol and water instead of water in the slaking of the lime. Retardation of the speed of slaking increased the grain size, and a series of products was obtained in which the particles varied from $2\,\mu$ to $300\,\mu$ average diameter.

International Association for Testing Materials.

THE following is a provisional list of the papers dealing with cements, lime and allied subjects to be read at the international congress of the International Association for Testing Materials, to be held in London from April 19 to 24. The Honorary Secretary, from whom further information may be obtained, is Mr. K. Headlam-Morley, of 28, Victoria Street, Westminster, S.W.1 :—

E. Rengade (France) : Some properties of Ciment Fondu.

A. Gessner and A. Frank (Czechoslovakia) : Standard tests with plastic mortar.

G. Haegermann (Germany) : The use of plastic mortar in cement tests.

A. Perfetti (Italy) : Laboratory tests on plastic mortars in relation to other tests suggested for acceptance of cements.

A. Brund (Sweden) : Quicker testing of cement and concrete by means of electric heating.

F. M. Lea (Great Britain) : Comparison of methods for measuring the heat evolution of cements.

B. Hellström (Sweden) : Methods of testing special cements for large dams.

P. H. Bates (U.S.A.) : Controlling the heat of hydration of cements.

G. Batta (Belgium) : The disintegration of concrete.

F. M. Lea (Great Britain) : Plaster mortar tests on pozzolanic cements.

H. Kühl (Germany) : Sea-water cements (chemical destruction of concrete).

F. Ferrari (Italy) : Comparison of the action of water on iron and iron-pozzolana cements.

M. Spindel (Austria) : Materials for waterproofing mortar and concrete.

F. Löventhal (Denmark) : The testing of waterproofing materials for concrete.

A. J. Newport (Great Britain) : Compacting mortar cubes by vibration.

R. Feret (France) : Porosity and permeability of concrete.

R. Feret (France) : Relation between the tensile and compressive strengths of mortar and concrete.

R. l'Hermite (France) : Experiments relating to the influence of physical factors on the set of cement and the binding of powdered minerals.

Determination of the Speed of Slaking Quicklime.

By P. P. BUDNIKOFF and L. GULINOVA.

As is well known, the period required for the complete slaking of lime is dependant on its chemical composition (purity), the duration and temperature of burning, and the particle size. Under normal conditions of slaking the chief factors are the amount of water mixed with the lime, the temperature at which the slaking is carried out, and the vigour with which the mixture is stirred. Practical experience shows that lime freshly slaked with an excess of water gives a finer product. Some workers are of the opinion that in the slaking process the CaO particles become covered with a hydrated layer which comes out of solution from the water due to the rising temperature. The presence of this surface on the lime particles retards their further slaking, and the hydration process proceeds slowly. In some circumstances complete slaking of the lime may take several months and sometimes even several years.
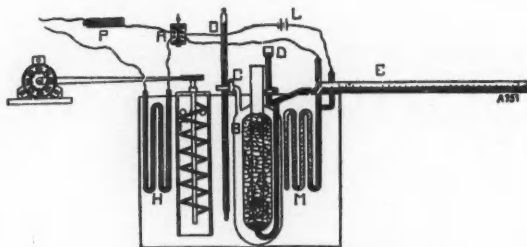

Fig. 1.—Diphenyl-Calorimeter.

A—Calorimeter.　B—Insulating container.　C—Vacuum lead.
D—Tube for filling with mercury.　E—Capillary.　F—Stirrer.
H—Heater.　　L—Accumulator.　　M—Thermoregulator.
O—Thermometer.　P—Resistance.　R—Relay.

In a discussion of this subject in *Tonindustrie Zeitung* (1936, p. 899) the authors state that various methods[1] have been suggested for accelerating the slaking of lime, including (1) Slaking with boiling water; (2) Vigorous stirring during the slaking; and (3) Slaking in flowing water.

The third method is, it is stated, of special interest and has the following advantages: (a) The possibility of removing any insufficiently burnt and over-burnt material (due to the difference in specific gravity), and of freeing the lime from various adulterants; and (b) The various soluble salts can be removed from the lime.

According to the type of salts present in the lime its properties can be altered, and there is often efflorescence in the plaster. Some salts act as retarders and others as accelerators of the hydration process. The authors have studied the

[1] W. Whitman and G. Davis, Slaking of Lime, *Ind. and Eng. Chem.*, Vol. 18, pp. 2, 118, 1926.

TABLE I.—ANALYSES OF RAW MATERIALS.

Material	Loss on ignition	In- soluble	Al_2O_3	Fe_2O_3	CaO	MgO
Limestone	43.16	1.20	0.11	0.74	54.65	0.07
Chalk	43.42	1.12	0.59	0.19	54.51	0.11
Chalk burned in a commercial kiln	0.26	1.47	1.10		97.09	0.12
Marble	44.46	—	—	0.06	55.09	0.21

influence of the burning temperatures of lime and of various salts on the speed of hydration. One of them has studied the speed of slaking of lime.[2]

In the research work now reported the calorimetric (diphenylmethane calorimeter) method was employed. The materials used were marble, chalk, and limestone, the chemical analyses of which are given in Table 1. For each test 10 g. of the finely-ground sample (no residue on a sieve with 10,000 meshes per square centimetre) were put in a platinum crucible which was heated in a crucible furnace to 900 deg. C., 1,000 deg. C. and 1,200 deg. C. ; the marble was also burnt at 1,650 deg. C. The highest temperature was maintained in all cases for two hours. After heating the sample was cooled slowly in the furnace until the temperature had fallen to 1,050 deg. C., when it was put into a desiccator. The burning temperature was measured by a standardised Pt-PtRh thermocouple, the hot junction of which was immersed in the material. The whole burning process took six hours and the temperature rise occupied $2\frac{1}{2}$ hours.

In order to obtain the speed of hydration of the lime, a diphenylmethane calorimeter[3] was used (*Fig.* 1) in which the amount of heat liberated on the hydration of the lime could be estimated. The tests were carried out as follows : 1 g. of finely-ground lime in a closed test-tube was placed in a thermostat and brought to the temperature of the calorimeter (about 23 deg. C. = melting point of diphenylmethane). The test-tube was then placed in the calorimeter (*a*), see *Fig.* 1. Temperature variations of 0.01 to 0.02 deg. C. were neglected. When the position of the mercury in the capillary of the calorimeter no longer varied, the lime was mixed with the water. 100 per cent. excess of water over that theoretically required was taken, i.e. for 1 g. CaO about 0.6 c.c. water was used. After the addition of water, the specimen was stirred in the test-tube with a glass rod. Observations of the position of the mercury in the capillary were made until it was certain that there was no further development of heat.

The results of the test are given in Tables 2 to 5. The amounts of heat liberated in relation to the time (speed of hydration) are given.in Tables 2, 3 and 4, and the temperatures corresponding to the total amount of heat in Table 5. Table 2 shows that marble burnt at 1,100 deg. C. has the greatest activity at

[2] P. P. Budnikoff, *Tonindustrie Zeitung*, Vol. 51, p. 737, 1927 ; and P. P. Budnikoff and A. Ja. Zvorykin, Speed of Slaking of Lime burned at various Temperatures, Mitt. des Ivanovo-Voznesenk Polytechnischen Institutes, Band VIII, 1924.

[3] P. P. Budnikoff and L. Gulinova, Method of Determining the Activity of Activated Silica Earth in Pozzolanic Materials, *Vortr. der Aked. d. Wiss. U.S.S.R.*, No. 7, p. 404, 1934 ; *Kolloidzeitschrift*, Bd. 70, 1935, p. 100.

TABLE 2.—HEAT OF HYDRATION OF LIME FROM MARBLE BURNED AT
VARIOUS TEMPERATURES.

Time		Burning temperature, deg. C.								
		900		1,000		1,100		1,200		1,650	
		Heat liberated in cal./g.									
hrs.	min	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount
	5	179	179	215	215	294	294	171.1	171.1	2.3	2.3
	10	33	212	38.7	253.7	25.8	319.8	66.5	237.6	2.8	5.1
	15	14	226	21.5	275.2	10.3	330.1	24.1	261.7	2.4	7.5
	20	2.8	228.5	5.2	280.4	0.4	330.5	2.6	264.3	7.5	15.0
	25	0.4	229.2	0	280.4	0	330.5	1.7	266.0	8.5	23.5
	30	0	229.2	—	,,	—	,,	1.3	267.3	8.9	32.4
	35	—	,,	—	,,	—	,,	0.8	268.1	8.9	41.3
	40	—	,,	—	,,	—	,,	0	,,	9.4	50.7
	45	—	,,	—	,,	—	,,	—	,,	14.1	64.8
	50	—	,,	—	,,	—	,,	—	,,	17.0	81.8
	55	—	,,	—	,,	—	,,	—	,,	18.8	100.6
1	00	—	,,	—	,,	—	,,	—	,,	19.7	120.3
1	10	—	,,	—	,,	—	,,	—	,,	15.0	135.0
1	20	—	,,	—	,,	—	,,	—	,,	12.2	147.5
1	30	—	,,	—	,,	—	,,	—	,,	9.4	156.9
1	40	—	,,	—	,,	—	,,	—	,,	9.2	166.1
1	50	—	,,	—	,,	—	,,	—	,,	8.1	174.2
2	00	—	,,	—	,,	—	,,	—	,,	8.2	182.4
2	10	—	,,	—	,,	—	,,	—	,,	5.3	187.7

TABLE 3.—HEAT OF HYDRATION OF LIME FROM LIMESTONE BURNED
AT VARIOUS TEMPERATURES.

Time		Burning temperature, deg. C.							
		900		1,000		1,100		1,200	
		Heat liberated, in cal./g.							
hr.	min.	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount
	5	46.4	46.4	48.6	48.6	39.6	39.6	24.9	24.9
	10	57.6	104.0	58.7	107.3	44.3	83.9	21.6	46.5
	15	86.4	190.4	86.6	193.9	50.0	133.9	18.9	65.4
	20	15.5	205.9	17.7	211.6	31.4	165.3	8.5	73.9
	25	2.6	208.5	3.4	215	20.6	185.9	8.5	82.4
	30	0	,,	0	,,	11.6	197.5	9.4	91.8
	35	0	,,	0	,,	7.7	205.2	25.4	117.2
	40	—	,,	—	,,	5.2	210.4	23.0	140.2
	45	—	,,	—	,,	2.1	212.5	9.9	150.1
	50	—	,,	—	,,	0.8	213.3	0.9	151.0
1	00	—	,,	—	,,	0	213.3	0.4	151.4

TABLE 4.—HEAT OF HYDRATION OF LIME FROM CHALK BURNED AT
VARIOUS TEMPERATURES.

Time	Burning temperature, deg. C.							
	900		1,000		1,100		1,200	
	Heat liberated, in cal./g.							
mins.	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount	In a 5-min. interval	Total amount
5	136	136	167.5	167.5	179	179	0	0
10	60	196	64.8	232.3	67	246	10	10
15	18	214	20.0	252.3	24	270	37	47
20	11	225	9.0	261.3	11	281	50	97
25	3	228	6.0	267.3	7	288	31	128
30	1	229	2.0	269.3	2	290	8	136
35	0.4	229.4	1	270.3	1	291	4	140
40	0	,,	0	,,	0	,,	3	143
45	—	,,	—	,,	—	,,	1	144
50	—	,,	—	,,	—	,,	0	,,

TABLE 5.—HEAT OF HYDRATION OF LIME FROM MARBLE, CHALK, AND
LIMESTONE BURNED AT VARIOUS TEMPERATURES.

Material	Temperature of burning, deg. C.				
	900	1,000	1,100	1,200	1,650
Marble	229.2	280.4	330.5	268.1	197
Chalk	229.4	270.3	290	144	—
Limestone	208.5	215	213.3	151	—

TABLE 6.

EFFECT OF VARIOUS SALT ADDITIONS TO THE HEAT OF HYDRATION (CAL/G.)
OF QUICKLIME.

| Time. hr. min.	H_2O	$Mg(OH)_2$	$CaSO_4$	$AlCl_3$	$BaCl_2$	$Ca(NO_3)_2$	$Na_2S_2O_3$	$Ca(CH_3COO)_2$	NH_4Cl	$MgCl_2$	$NaCl$	$CaCl_2$	$NaOH$
10	20.6	2	10	39.0	21.6	6	14	118	218	63	108	50	16
20	20.6	26	32	199.0	189.6	70	190	230	243	227	224	252	108
30	203.6	140	76	225.0	226.3	165	230	238	256	252	254	285	234
40	226.6	286	126	226.5	227.5	205	236	238	256	258	260	287	295
50	228.6	210	158	226.5	227.5	225	236	238	256	258	260	287	326
1 00	229.6	214	190	226.5	227.5	233	236	238	256	258	260	287	335
1 10	229.6	216	222	226.5	227.5	233	236	238	256	258	260	287	337
1 20	229.6	216	222	226.5	227.5	233	236	238	256	258	260	287	337
1 30	229.6	216	222	226.5	227.5	233	236	238	256	258	260	287	337
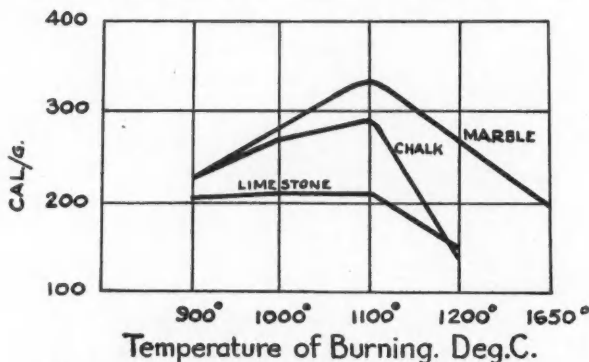
Fig. 2.—Heat of Hydration of Lime from Marble,
Chalk and Limestone.

330.5 cal. in twenty-five minutes ; marble burnt at 900 deg. C. liberates 229.2 cal. in the same time ; and marble burnt for twenty-five minutes at 1,000 deg. C. liberates 280.4 cal. Burning of the marble at a high temperature causes a drop in the activity of the product. Table 3 shows that the greatest activity of lime from the burning of limestone is obtained at 1,100 deg. C., which is understandable because limestone is less pure than marble.
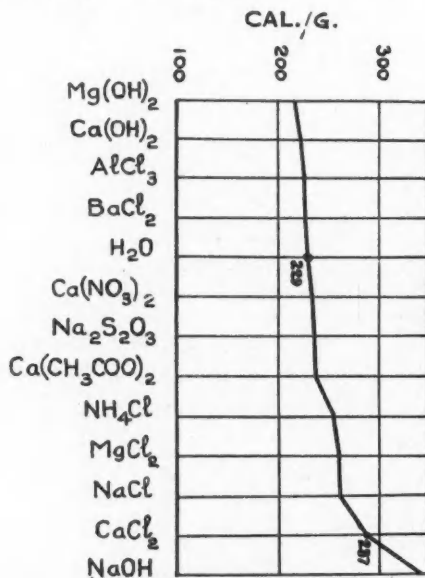

Fig. 3.—Heat of Hydration of Lime with the addition
of 1 per cent. of various salts.

The results obtained using lime obtained from chalk are given in Table 4. As in the case of marble, the optimum burning temperature is 1,100 deg. C. At this temperature 288 cal. were liberated in 25 minutes and at a burning temperature of 1,000 deg. C. only 267.3 cal. were liberated in the same time. A further rise in the burning temperature causes a reduction in the activity of the lime obtained. Table 5 gives a review of the total amounts of heat in cal./g. liberated in the hydration of the various specimens, and in *Fig.* 2 these are set out graphically.

In a second series of tests, the influence of additions (1 per cent.) on the heat of hydration of lime was investigated. For this purpose lime made from chalk burnt at about 1,100 deg. C. in a commercial kiln was used. The results are given in Table 6. The addition of a salt in most cases caused an acceleration of the hydrating process. In this connection calcium chloride is of special interest, since with this 285 cal./g. were liberated in thirty minutes, which is nearly equal to the total heat of hydration. *Fig.* 3 shows the effects of various salts on the total heat liberated. The accelerating action of certain salts appears to be due to their dispersing action and hence the greater solubility of the lime.

This acceleration of the slaking of lime by salts may have practical value in the manufacture of sand-lime bricks or lime-clay bricks in high pressure steam, and also of heat-resisting products.

Weighing in the Cement and Lime Industries.

AN automatic weighing plant with a daily output of 450 tons of cement is illustrated in *Fig.* 1. These machines weigh continuously without manual operation, and also automatically provide data for the " flow sheet."

At the first stage, that of proportioning, four machines of different capacities are installed beneath bunkers containing the ingredients and discharge simul-
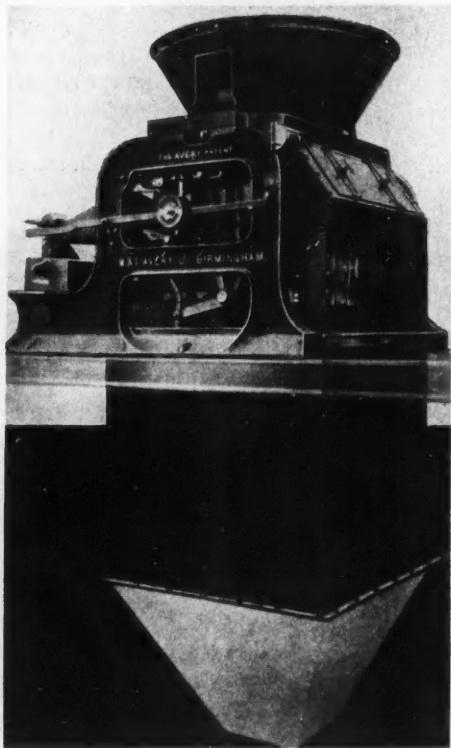

Fig. 1.

taneously on to a band conveyor carrying the constituents to a mixer and storage hopper prior to calcining. In this installation, from the kiln, the clinker is weighed hot on another automatic weigher before being ground.

The powdered cement is weighed into the storage silos through two totally-enclosed automatic bulk weighers. These are fitted with an agitator inside the
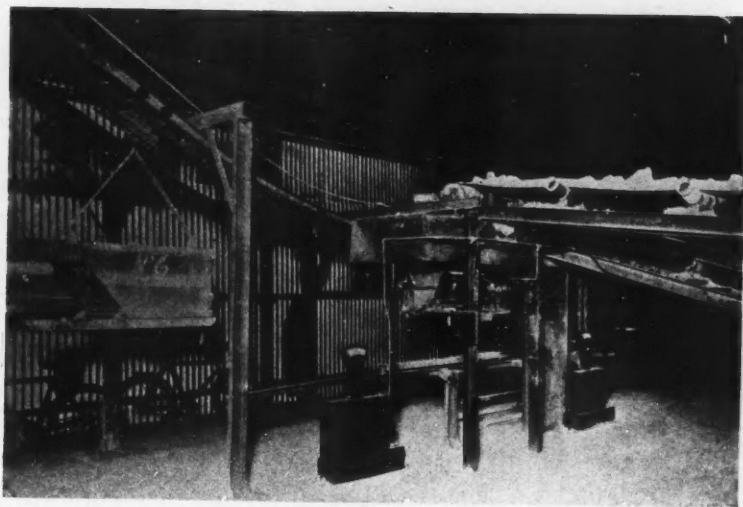
Fig. 2.

Fig. 3.

feed hopper to ensure a continuous and even flow, while the weigh hoppers are circular in shape to give a clean discharge. Various devices prevent the escape of dust into the atmosphere and on the working parts of the scale, and weighings are accurate to within one-quarter per cent.

In another installation the ingredients are fed from the storage bins on belt conveyors into skips travelling to the kilns (*Figs.* 2 and 3). Between the conveyor and skip is a self-indicating scale connected to a weigh hopper. The conveyor is started, the hopper is filled to a predetermined weight, and a switch,
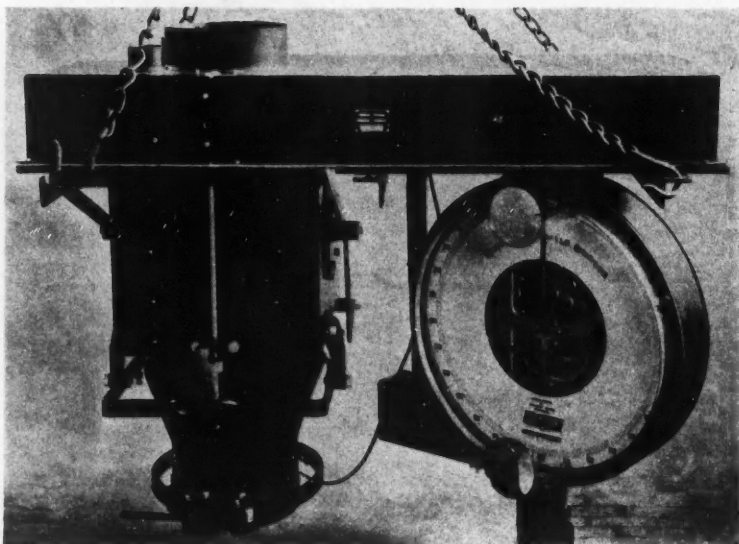
Fig. 4.

operated by the scale, cuts out the motor driving the conveyor. The hopper then discharges into a skip which has by this time travelled beneath it, the steelyard of the scale falls, and the conveyor motor is restarted. The electrically-interlocked system prevents any operation taking place at the incorrect time and enables the whole cycle to continue automatically.

A special machine has been evolved for weighing powdered materials directly from storage bins or hoppers into sacks. This machine is equipped with a chute mounted directly under the storage hopper and terminating in a hand-controlled radial valve. The valve is enclosed in a dust-box to which the sack chute is flexibly attached, this in turn being mounted on the weighing machine. Two views of this machine are given in *Figs.* 4 and 5. A special feature is a patented
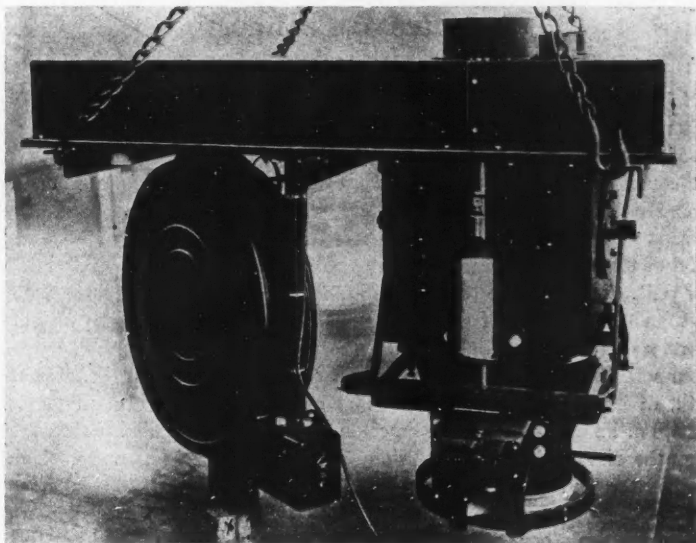
Fig. 5.

sack grip which facilitates the securing of the sack to the chute by means of a simple adjustable latch. A secure grip of the sack is ensured at all times, and the whole flow line of the material is dust proof.

With the sack in position, the feed valve is opened and the weight of the falling material is progressively indicated by a pointer moving round a dial in view of the operator, who thus has absolute control over the feed and can reduce its volume as the predetermined weight is approached. A counter is fitted which is partially operated by the pointer reaching the predetermined load, and completed by the opening of the sack grip, so that it is impossible to operate the counter either by misuse of the scale or the sack grip.

The machines illustrated and described were supplied by Messrs. W. and T. Avery, Ltd.

Notes on Lime.

By D. B. BUTLER, Assoc.M.Inst.C.E., M.Inst.Struct.E., F.C.S.

THE following notes are intended only as a very elementary introduction to the chemistry and manufacture of the material.

From the point of view of the chemist, lime is pure calcium oxide (CaO), but in the commercial sense of the term it covers a wide range of materials varying enormously, both in their chemical and physical properties, according to the calcareous content of the raw materials from which they are produced. At one end of the scale there are pure limes containing, when freshly burned, about 99 per cent. of actual lime (CaO), and at the other very impure limes with little more than 50 per cent. of CaO, the remainder usually consisting of clay constituents such as silica and alumina.

Commercial lime is produced by burning at a good red heat, i.e. about 1,100 deg. C., of limestones, chalks, and other calcareous formations, converting the carbonate of lime content of the limestone or chalk into calcium oxide or quicklime by the dissociation and expulsion of the carbonic acid as a gas. This may be represented by the chemical formula :

$$CaCO_3 = CaO + CO_2$$

i.e. the calcium carbonate is split up into quicklime and carbonic acid. With argillaceous or clayey limestones and chalks burning also causes some degree of chemical combination between the lime and the clay constituents, converting the latter from insoluble to soluble compounds, and thus rendering them more active as regards setting and hardening.

For industrial and agricultural purposes the purest limes are the most suitable, since their efficiency depends upon their calcium oxide (CaO) content ; any clay constituents that may be present are of no value, and are more or less of an adulteration from the users' point of view.

For building and structural purposes, however, the value of the limes for certain purposes depends upon the amount of silica and alumina they contain, which impart to them a certain amount of setting activity.

Pure white limes have, by themselves, no setting properties in the strict sense of the term ; their hardening as mortars is due first of all to their drying out, in the same way that a mortar composed of mud and sand hardens by drying out. This is followed by a very slow process of further hardening, due to the gradual combination of the lime in the mortar with the carbonic acid (CO_2) in the atmosphere to form carbonate of lime, or what may be described as a slow process of recarbonation. Pure white lime is also slightly soluble in water, and has no hydraulic properties, i.e. ability to set and harden under water, which is an important feature with the impure limes, to a greater or lesser extent according to the proportion and nature of their clay content.

For building and constructive purposes, therefore, commercial limes are generally classified according to their hydraulic properties, following closely the nomenclature adopted by M. Vicat of rather more than a century ago ; this

is as follows : (1) Fat or non-hydraulic limes ; (2) Feebly hydraulic limes ; (3) Hydraulic limes ; (4) Eminently hydraulic limes. We will deal first with the chalk limes, i.e. those produced from the various chalk formations.

The White or Upper Chalk is nearly pure carbonate of lime, with little argillaceous or clay constituents in the form of silica and alumina, as will be seen from the writer's analysis of a sample recently taken by him from a quarry in the South Downs :

	Per cent.
Water and organic matter..	0.23
Silica	0.90
Alumina	0.44
Oxide of iron	0.40
Carbonate of lime	96.77
Carbonate of magnesia	0.63
Sulphuric anhydride	nil
Alkalis and loss	0.63
	100.00

The calculated composition of the lime produced by burning this chalk would be as follows, without making allowance for any contamination which might be caused by the ash of the fuel used for calcination.

	Per cent.
Silica	1.59
Alumina	0.79
Oxide of iron	0.71
Lime ..	95.30
Magnesia	0.53
Sulphuric anhydride	nil
Alkalis and loss	1.08
	100.00

Although they vary slightly as regards clay content in different localities, the lime from the Upper Chalk may generally be classified under the heading (1), i.e. fat or non-hydraulic lime.

Next in geological order, and lying beneath the White Chalks, are the Lower or Grey Chalks, most of which produce what is commercially known as greystone lime. An analysis by the writer of this chalk, taken from the same locality as the first-mentioned White Chalk, gave the following results, beside which is given the calculated composition of the lime it would produce.

	Chalk. Per cent.	Lime. Per cent.
Water and organic matter..	0.38	—
Silica	5.04	8.55
Alumina	1.74	2.95
Oxide of iron	0.30	0.51
Carbonate of lime	91.72	—
Lime ..	—	87.17
Carbonate of magnesia	0.65	—
Magnesia	—	0.53
Sulphuric anhydride	nil	nil
Alkalis and loss	0.17	0.29
	100.00	100.00

It will be observed that this chalk is considerably less pure than the White Chalk, i.e. it contains more hydraulic constituents in the form of silica and alumina.

The **Grey Chalks** also vary as regards clay content, and may be said to range from (2) to (3) in Vicat's classification, i.e. from feebly hydraulic to hydraulic limes. The following is an analysis of an ordinary greystone lime as given by the Greystone Lime Burners' Association :

|	Per cent.
Silica	9.20
Ferric oxide and alumina	4.85
Lime	81.37
Magnesia	0.59
Sulphate of lime	0.58
Alkalis and loss	0.35
Loss on ignition	3.06
	100.00

This corresponds fairly closely with that of the Lower Chalk product.

Of still lower geological formation, and lying beneath the Lower or Grey Chalks, are those which have a still greater clay content, and thus produce, according to (4) of Vicat's classification, eminently hydraulic limes. The following is the composition of one of these chalks, and the calculated composition of the lime it would produce when freshly burned.

	Chalk. Per cent.	Lime. Per cent.
Water and organic matter	1.78	—
Silica	17.28	26.46
Alumina	4.43	6.78
Oxide of iron	0.95	1.47
Carbonate of lime	73.46	—
Lime	—	62.98
Carbonate of magnesia	1.11	—
Magnesia	—	0.81
Sulphuric anhydride	nil	nil
Alkalis and loss	0.98	1.50
	100.00	100.00

Limes produced from limestone also range from practically pure non-hydraulic limes such as are produced from the limestones in Derbyshire and elsewhere to eminently hydraulic limes produced from the Lias formations of Warwickshire, South Wales, etc. The limestones of the Blue Lias formations are generally interstratified with layers of more or less calcareous shale ; these limestone beds range in thickness from 2 or 3 in. to about 1 ft., each layer varying considerably in composition. According to analyses made by the writer a few years ago the carbonate of lime content ranges from about 75 to 84 per cent. The following is a typical analysis of Blue Lias lime intended for general use :

	Per cent.
Water and carbonic anhydride	3.85
Silica	17.53
Alumina	6.83
Oxide of iron	2.87
Lime	65.84
Magnesia	1.00
Sulphuric anhydride	1.36
Insoluble matter	0.50
Alkalis and loss	0.22
	100.00
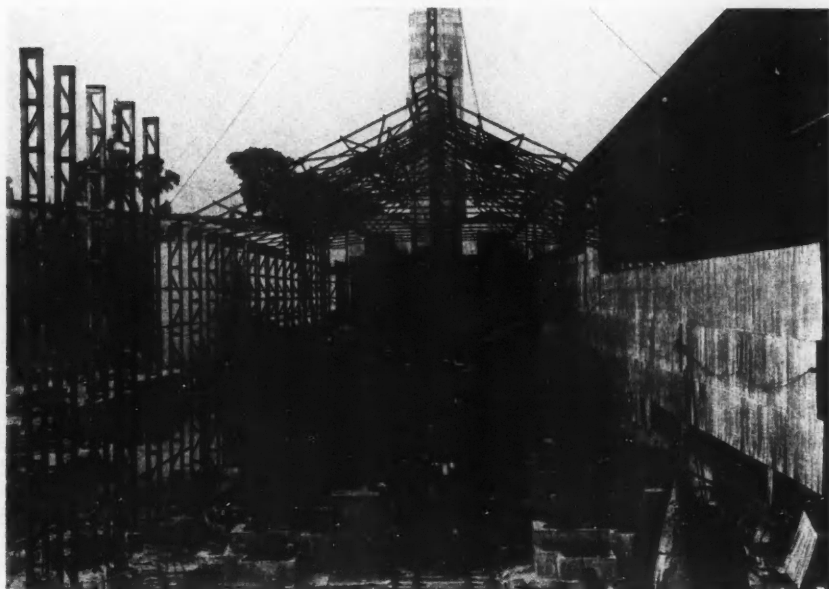
Wherever limestone or chalk is found lime kilns of a primitive nature may frequently be noticed supplying lime for local use, but the greater proportion of the manufacture is produced on a large scale at factories specially designed and equipped for the purpose.

Limestones and chalks on burning not only undergo chemical changes by conversion of the carbonate of lime into calcium oxide or quicklime, but the changes in their condition and appearance are scarcely less marked. For instance hard limestones and chalks become more or less soft and friable after burning, while their colour may range from almost white with pure chalks to various shades of yellowish brown with more impure varieties, the amount of coloration being generally due to the oxide of iron content.

Lime has to be slaked before it is mixed with sand or other gritty siliceous material to form mortar, because when the CaO in the freshly burned lime comes into contact with moisture it increases enormously in bulk, and evolves considerable heat owing to the chemical reaction in the formation of calcium hydrate ; if it were not thoroughly slaked before use it would swell and become a disruptive, instead of a binding material. Limes slake on the addition of water quickly or slowly according to their clay content, the pure non-hydraulic limes slaking very rapidly while the eminently hydraulic limes slake very slowly ; whatever method of slaking be adopted it is essential that all the quicklime present should be converted into hydrate, or the stability of volume of the resulting mortar will be jeopardised. For slaking Blue Lias lime the following method is recommended. The lime should be tipped on the mixing boards, sprinkled with water, covered with the sand to be used, and left for 24 hours to slake ; the lime and sand should then be thoroughly mixed, after which water may be added as required to make the mortar. Any unslaked pieces may be removed and put into the middle of the next heap to be slaked.

Lime until recent years was marketed either in the condition in which it came from the kiln (lump lime) or after a certain amount of pulverisation (ground lime) ; the former was delivered loose, and the latter in sacks. To these hydrated lime has been added during the past few years, and is already slaked or hydrated and delivered in sacks in powder form. This method of marketing was first adopted with the non-hydraulic fat limes or the feebly hydraulic limes only, but has recently been extended to include the eminently hydraulic limes such as Blue Lias. Hydrated limes have the advantage of being ready for immediate use, and, if properly prepared, immunity from possible subsequent trouble due to imperfect slaking.

In spite of its importance as a building material, there is as yet no British standard specification for limes, although one has been in preparation for some time past. To be of the fullest service to manufacturers and users the specification should clearly define the chemical constituents and physical properties of each class of lime and ensure that the user obtains a properly prepared material.